

FORM PTO-1390 (Modified) (REV'11-2000)		U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE		ATTORNEY'S DOCKET NUMBER <b>208608US0PCT</b>	
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371				U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR <i>627975</i>	
INTERNATIONAL APPLICATION NO. <b>PCT/EP99/08850</b>	INTERNATIONAL FILING DATE <b>18 November 1999</b>	PRIORITY DATE CLAIMED <b>26 November 1998</b>			
TITLE OF INVENTION <b>HYDROGELS CAPABLE OF ABSORBING AQUEOUS FLUIDS</b>					
APPLICANT(S) FOR DO/EO/US <b>DANIEL Thomas et al.</b>					
<p>Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:</p> <ol style="list-style-type: none"> <li>1. <input checked="" type="checkbox"/> This is a <b>FIRST</b> submission of items concerning a filing under 35 U.S.C. 371.</li> <li>2. <input type="checkbox"/> This is a <b>SECOND</b> or <b>SUBSEQUENT</b> submission of items concerning a filing under 35 U.S.C. 371.</li> <li>3. <input checked="" type="checkbox"/> This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (24) indicated below.</li> <li>4. <input checked="" type="checkbox"/> The US has been elected by the expiration of 19 months from the priority date (Article 31).</li> <li>5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371 (c) (2))             <ol style="list-style-type: none"> <li>a. <input type="checkbox"/> is attached hereto (required only if not communicated by the International Bureau).</li> <li>b. <input checked="" type="checkbox"/> has been communicated by the International Bureau.</li> <li>c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US).</li> </ol> </li> <li>6. <input checked="" type="checkbox"/> An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).             <ol style="list-style-type: none"> <li>a. <input checked="" type="checkbox"/> is attached hereto.</li> <li>b. <input type="checkbox"/> has been previously submitted under 35 U.S.C. 154(d)(4).</li> </ol> </li> <li>7. <input checked="" type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))             <ol style="list-style-type: none"> <li>a. <input type="checkbox"/> are attached hereto (required only if not communicated by the International Bureau).</li> <li>b. <input type="checkbox"/> have been communicated by the International Bureau.</li> <li>c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired.</li> <li>d. <input checked="" type="checkbox"/> have not been made and will not be made.</li> </ol> </li> <li>8. <input type="checkbox"/> An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).</li> <li>9. <input checked="" type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).</li> <li>10. <input type="checkbox"/> An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).</li> <li>11. <input type="checkbox"/> A copy of the International Preliminary Examination Report (PCT/IPEA/409).</li> <li>12. <input checked="" type="checkbox"/> A copy of the International Search Report (PCT/ISA/210).</li> </ol> <p><b>Items 13 to 20 below concern document(s) or information included:</b></p> <ol style="list-style-type: none"> <li>13. <input type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98.</li> <li>14. <input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.</li> <li>15. <input checked="" type="checkbox"/> A <b>FIRST</b> preliminary amendment.</li> <li>16. <input type="checkbox"/> A <b>SECOND</b> or <b>SUBSEQUENT</b> preliminary amendment.</li> <li>17. <input type="checkbox"/> A substitute specification.</li> <li>18. <input type="checkbox"/> A change of power of attorney and/or address letter.</li> <li>19. <input type="checkbox"/> A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.</li> <li>20. <input type="checkbox"/> A second copy of the published international application under 35 U.S.C. 154(d)(4).</li> <li>21. <input type="checkbox"/> A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).</li> <li>22. <input type="checkbox"/> Certificate of Mailing by Express Mail</li> <li>23. <input checked="" type="checkbox"/> Other items or information:</li> </ol> <p><b>Notice for Consideration of Documents Cited in International Search Report</b>  <b>Notice of Priority</b>  <b>PCT/IB/304</b></p>					

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR  
09/831915INTERNATIONAL APPLICATION NO.  
PCT/EP99/08850ATTORNEY'S DOCKET NUMBER  
208608US0PCT

24. The following fees are submitted:

**BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) :**

<input type="checkbox"/> Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO .....	\$1000.00
<input checked="" type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO .....	\$860.00
<input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO .....	\$710.00
<input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) .....	\$690.00
<input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) .....	\$100.00

**CALCULATIONS PTO USE ONLY****ENTER APPROPRIATE BASIC FEE AMOUNT =**

\$860.00

Surcharge of \$130.00 for furnishing the oath or declaration later than months from the earliest claimed priority date (37 CFR 1.492 (e)).

 20     30

\$0.00

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	
Total claims	12 - 20 =	0	x \$18.00	\$0.00
Independent claims	1 - 3 =	0	x \$80.00	\$0.00

Multiple Dependent Claims (check if applicable).

 \$0.00**TOTAL OF ABOVE CALCULATIONS =**

\$860.00

 Applicant claims small entity status. (See 37 CFR 1.27). The fees indicated above are reduced by 1/2.

\$0.00

**SUBTOTAL =**

\$860.00

Processing fee of \$130.00 for furnishing the English translation later than months from the earliest claimed priority date (37 CFR 1.492 (f)).

 20     30

+ \$0.00

**TOTAL NATIONAL FEE =**

\$860.00

Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable).

 \$0.00**TOTAL FEES ENCLOSED =**

\$860.00

Amount to be: refunded	\$
charged	\$

- a.  A check in the amount of \$860.00 to cover the above fees is enclosed.
- b.  Please charge my Deposit Account No. \_\_\_\_\_ in the amount of \_\_\_\_\_ to cover the above fees. A duplicate copy of this sheet is enclosed.
- c.  The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 15-0030. A duplicate copy of this sheet is enclosed.
- d.  Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. **Credit card information should not be included on this form.** Provide credit card information and authorization on PTO-2038.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:



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Surinder Sachar  
Registration No. 34,423

SIGNATURE

Norman F. Oblon

NAME

24,618

REGISTRATION NUMBER

May 24 2001

DATE

09/03/1915  
JC18 Rec'd PCT/PTO 25 MAY 2001

208608US-0 PCT

IN THE UNITED STATES PATENT & TRADEMARK OFFICE

IN RE APPLICATION OF : :

THOMAS DANIEL ET AL : ATTN: APPLICATION DIVISION

SERIAL NO: NEW U.S. PCT APPLN :  
(BASED ON PCT/EP99/08850)

FILED: HEREWITH : :

FOR: HYDROGELS CAPABLE OF  
ABSORBING AQUEOUS FLUIDS

PRELIMINARY AMENDMENT

ASSISTANT COMMISSIONER FOR PATENTS  
WASHINGTON, D.C. 20231

SIR:

Prior to examination on the merits, please amend the above-identified application as follows.

IN THE CLAIMS

Please amend the claims as shown on the marked-up copy following this amendment to read as follows.

4. (Amended) Polymers as claimed in claim 1, wherefor the acidic addition polymers are neutralized with mixtures of alkali metal silicates and alkali metal hydroxides.

5. (Amended) Polymers as claimed in claim 1, wherefor the acidic addition polymers are neutralized with mixtures of alkali metal silicates and alkali metal carbonates.

6. (Amended) Polymers as claimed in claim 1, wherefor the acidic addition polymers are neutralized to a pH of from 3.5 to 9.0.

7. (Amended) Polymers as claimed in claim 1, wherefor the drying temperatures are in the range from 40°C to 300°C.

8. (Amended) Polymers as claimed in claim 1, characterized by a GLP gel permeability of not less than  $25 \times 10^{-7}$  cm<sup>3</sup>sec/g at a polymer pH of from 5.0 to 9.0.

9. (Amended) Polymers as claimed in claim 1, characterized by a GLP gel permeability of not less than  $4 \times 10^{-7}$  cm<sup>3</sup>sec/g at a polymer pH of less than 5.0.

**Marked-Up Copy**

Serial No: \_\_\_\_\_

Amendment Filed on:  
\_\_\_\_\_

**IN THE CLAIMS**

--4. (Amended) Polymers as claimed in [any of claims 1 to 3] claim 1, wherefor the acidic addition polymers are neutralized with mixtures of alkali metal silicates and alkali metal hydroxides.

5. (Amended) Polymers as claimed in [any of claims 1 to 3] claim 1, wherefor the acidic addition polymers are neutralized with mixtures of alkali metal silicates and alkali metal carbonates.

6. (Amended) Polymers as claimed in [any of claims 1 to 5] claim 1, wherefor the acidic addition polymers are neutralized to a pH of from 3.5 to 9.0.

7. (Amended) Polymers as claimed in [any of claims 1 to 6] claim 1, wherefor the drying temperatures are in the range from 40°C to 300°C.

8. (Amended) Polymers as claimed in [any of claims 1 to 7] claim 1, characterized by a GLP gel permeability of not less than  $25 \times 10^{-7}$  cm<sup>3</sup>sec/g at a polymer pH of from 5.0 to 9.0.

9. (Amended) Polymers as claimed in [any of claims 1 to 7] claim 1, characterized by a GLP gel permeability of not less than  $4 \times 10^{-7}$  cm<sup>3</sup>sec/g at a polymer pH of less than 5.0.--

REMARKS

Claims 1-12 are active in the present application. Claims 4-9 have been amended to remove multiple dependencies. No new matter is added. An action on the merits and allowance of claims is solicited.

Respectfully submitted,

OBLON, SPIVAK, McCLELLAND,  
MAIER & NEUSTADT, P.C.



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Hydrogels capable of absorbing aqueous fluids

Description

5

The present invention relates to hydrogels prepared using silicates, a process for their preparation and their use for absorbing aqueous fluids.

10 The inventive hydrogels capable of absorbing aqueous fluids are water-insoluble carboxylate polymers which contain a polysilicate matrix and are capable of swelling and forming hydrogels to absorb aqueous fluids and body fluids, for example urine or blood, and to retain the absorbed fluid under a certain pressure.

15

To prepare polymers capable of forming hydrogels having a particularly high absorption capacity, a high gel strength and high absorbency under load, the addition polymer particles may be subjected to a subsequent surface treatment, postcrosslinking.

20

Postcrosslinking is preferably effected using compounds known as crosslinkers which contain two or more groups capable of forming covalent bonds with the carboxyl groups of the hydrophilic polymers, see EP-A-0 349 240.

25

Known crosslinkers are polyglycidyl ethers, haloepoxy compounds, polyols, polyamines or polyisocyanates. DE-A-3 314 019, EP-A-0 317 106 and DE-A-3 737 196 further mention polyfunctional aziridine compounds, alkyl di(tri)halides and oil-soluble 30 polyepoxy compounds as crosslinkers.

According to DE-A-4 020 780 improved absorbency under load is obtained by surface crosslinking treatment of the polymer with from 0.1 to 5% by weight of alkylene carbonate.

35

The subsequent addition of finely divided amorphous silicas such as AERIL® or CAB-O-SIL® or bentonites atop the surface of powders or granules to finish absorbent polymers is likewise known.

EP-A-0 450 923, EP-A-0 450 922, DE-A-3 523 617, US-A-5 140 076

40 and US-A-4 734 478 teach the addition of silica in the course of the process of surface postcrosslinking dry powders of absorbent polymers using carboxyl-reactive crosslinkers. US-4 286 082 describes the use of mixtures of silica with absorbent polymers for use in hygiene articles. JP 65 133 028A and JP 61 017 542B

45 describe blends of hydrophobic silica types with absorbent polymers. EP-A-0 341 951, US-A-4 990 338 and US-A-5 035 892 describe the use of silica in the production of antimicrobially

finished absorbent polymers. US-A-4 535 098 and EP-A-0 227 666 finally describe the addition of colloidal carrier substances based on silica to enhance the gel strength of absorbent polymers.

5

These "dry" blends, where the additives merely adhere to the surface of the polymer, however, modify the characteristic profile of the absorbent hydrogels, for example rendering them hydrophilic or hydrophobic, which primarily affects the

10 absorption rate. In addition, the gel strength of the swollen particles is also increased in part, but it is a common feature of all these polymers that the permeability through swollen gel is unsatisfactory, regardless of the acquisition time.

15 It is an object of the present invention to provide novel hydrogels possessing in particular improved mechanical stability and enhanced permeability of the swollen gel particles. This object is to be achieved without any of the customary crosslinkers.

20

We have found that this object is achieved, surprisingly, by the use of silicates which are added to the hydrogels before, during or after the polymerization reaction, but before the drying of the hydrogels.

25

The present invention accordingly provides hydrogels capable of absorbing aqueous fluids, prepared by polymerization of olefinically unsaturated carboxylic acids or derivatives thereof, wherefor the polymerization reaction mixture is admixed with an 30 alkali metal silicate of the general formula I



where M is an alkali metal and n is generally from 0.5 to 4, 35 before, during or after the polymerization reaction and before drying and the hydrogel thus obtained is then dried at elevated temperature.

The compounds of the formula I are preferably used in amounts of 40 from 0.05 to 100%, particularly preferably from 1 to 70%, especially from 1 to 40%, specifically from 1 to 20%, by weight, reckoned on  $\text{SiO}_2$  and based on the total monomer weight; that is, the use of 100% by weight of compounds of the formula I 45 represents the use of equal weights of monomers and silicates. M is preferably sodium or potassium.

The preparation of these alkali metal silicates is common knowledge and is effected by reacting aqueous alkali with  $\text{SiO}_2$  or by fusing quartz sand with alkali metal carbonates at high temperatures in a molar ratio of from 1:2 to 4:1. The cooled 5 glassy melts are soluble in water and are therefore also known as "waterglasses".

The commercially available aqueous solutions of alkali metal silicates of the formula I are produced by dissolving the solid 10 melts in superheated water under pressure.

The aqueous solutions of alkali metal silicates (waterglasses) give an alkaline reaction as a consequence of partial hydrolysis. As well as alkali metal and hydroxide ions, they also contain 15 monosilicate ions,  $\text{HSiO}_4^{3-}$ ,  $\text{H}_2\text{SiO}_4^{2-}$  and  $\text{H}_3\text{SiO}_4^-$  and also cyclic and three-dimensionally crosslinked polysilicate ions.

On acidification, aqueous alkali metal silicate solutions form spherical amorphous silicas, known as silica sols, which tend to 20 form a gellike mass (silica hydrogels). It comprises a polycondensate of spherical silicas which is pervaded by numerous water-filled pores. Drying of the hydrogel at relatively high temperatures gives solid silica gels, specifically "silica aerogels".

25 Useful olefinically unsaturated carboxylic acids or derivatives thereof include in particular acrylic acid, methacrylic acid, crotonic acid, 2-acrylamido-2-methylpropanesulfonic acid and -phosphonic acid, vinylphosphonic acid, vinylphosphonic 30 monoesters, salts thereof, acrylamide, N-vinylamides or mixtures thereof. Preference is given to acrylic acid and its salts.

The preparation and use of such polymers capable of hydrogel formation is described in numerous patent specifications such as 35 EP-A-0 316 792, EP-A-0 400 283, EP-A-0 343 427, EP-A-0 205 674 and DE-A-4 418 818.

The polymerization is preferably carried out in a homogeneous phase, for example in an aqueous solution, as a gel 40 polymerization.

The polymerization, as will be general knowledge, can be initiated by free radical formers, for example organic or inorganic peroxides and also azo compounds. Examples are benzoyl 45 peroxide, tert-butyl hydroperoxide, cumene hydroperoxide,

$(\text{NH}_4)_2\text{S}_2\text{O}_8$ ,  $\text{K}_2\text{S}_2\text{O}_8$ ,  $\text{H}_2\text{S}_2\text{O}_8$ ,  $\text{H}_2\text{O}_2$  or azodiisobutyronitrile. Redox systems are also very useful as polymerization initiators.

The polymerization may finally also be initiated by means of high energy radiation.

Preferably, the acidic addition polymers are neutralized with mixtures of alkali metal silicates and alkali metal hydroxides, preferably in the form of the aqueous solutions, after the 10 polymerization. It is likewise preferable to neutralize the acidic addition polymers with mixtures of alkali metal silicates and alkali metal carbonates.

The acidic addition polymers are preferably neutralized to a pH 15 in the range from 3.5 to 9.0, especially 4.0-6.5.

The temperatures for the subsequent drying of the hydrogels are preferably in the range from 40°C to 300°C, especially in the range from 120°C to 220°C.

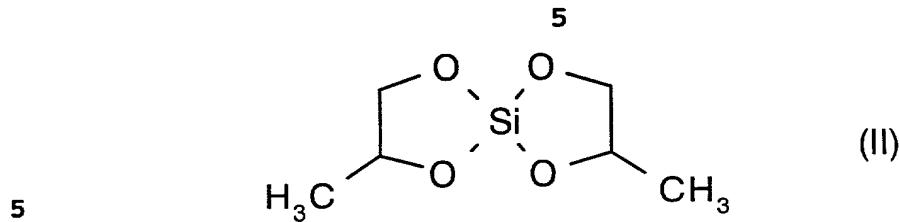
20 At a polymer pH of from 5.0 to 9.0, the gel permeability, measured as GLP, is preferably at least  $25 \times 10^{-7}$  cm<sup>3</sup>sec/g, particularly preferably at least  $45 \times 10^{-7}$  cm<sup>3</sup>sec/g, especially at least  $60 \times 10^{-7}$  cm<sup>3</sup>sec/g.

25 At a polymer pH of less than 5.0, the gel permeability, measured as GLP, is in particular at least  $4 \times 10^{-7}$  cm<sup>3</sup>sec/g, preferably at least  $10 \times 10^{-7}$  cm<sup>3</sup>sec/g, particularly preferably at least  $20 \times 10^{-7}$  cm<sup>3</sup>sec/g.

30 The hydrogels of the invention are very useful as absorbents for aqueous fluids, for example for absorbing aqueous solutions, dispersions and emulsions, especially for absorbing body fluids such as blood and urine, for producing articles for absorbing 35 aqueous fluids and for producing absorbent hygiene articles.

Hydrogels of the invention which are based on acrylic acid are particularly useful as superabsorbent polymers (SAPs) for use in hygiene articles, for example diapers, tampons or sanitary 40 napkins, for which they may be partly present as alkali metal or amine salt. Neutralization is effected according to the invention by addition of alkali metal silicates.

Postcrosslinking, especially in the surface, with mono-, bis- and 45 polyoxazolidinones, with the cyclic ester of propanediol with silicic acid of the formula II



or with compounds which contain at least 2 carboxyl-reactive functional groups in the molecule, such as di-, tri- or polyepoxides, for example ethylene glycol diglycidyl ether or 10 haloepoxy compounds or polyamine compounds and also polyhydric alcohols such as ethylene glycol, propylene glycol, trimethylolpropane, substantially improves performance with regard to absorbency under load.

- 15 The polymer of the invention has a harder, more crystalline character in the swollen state, which not only suppresses stickiness but also results in improved fluid transportation or drainage, especially under a restraining force.
- 20 The examples hereinbelow illustrate the preparation and properties of polymers according to the invention and the test methods for determining the properties of the hydrogels.

#### Test methods

- 25 Centrifuge retention capacity (CRC):

This method determines the free swellability of the hydrogel in a teabag.  $0.2000 \pm 0.0050$  g of dried hydrogel are welded into a 30 teabag (format: 60 mm x 60 mm, Dexter 1234T paper) and soaked for 30 minutes in a 0.9% by weight sodium chloride solution. The teabag is then centrifuged for 3 min in a commercially available spin dryer (1400 rpm, basket diameter 230 mm). The absorbed amount of liquid is determined by weighing the centrifuged 35 teabag.

To allow for the absorption capacity of the teabag itself, the test is also carried out on a teabag without water-absorbent hydrogel, as a blank.

- 40 Retention CRC [g/g] = (final weight - blank value - starting weight)/starting weight

where

45

## 6

- final weight                   is the wet weight of the swollen and centrifuged teabag plus contents
- starting weight               is the dry sample weight and
- 5                              blank value                   is the wet weight of the empty teabag after centrifuging.

## Absorbency under load:

- 10                             0.1600 ± 0.0050 g of dry hydrogel are uniformly distributed on the sieve base of a measuring cell. The measuring cell consists of a Plexiglas cylinder 33 mm in height and 25 mm in diameter, to which a 36 micron steel mesh has been adhered as base.
- 15                             A covering plate is placed on top of the uniformly distributed hydrogel and loaded with an appropriate weight. The cell is placed in a Petri dish 10 mm in height and 100 mm in diameter, which contains 13 ml of 0.9% by weight sodium chloride solution.
- 20                             The hydrogel is allowed to absorb the salt solution for 60 min. The complete cell with the swollen gel is then removed from the Petri dish and after the weight has been removed the apparatus is reweighed.

25 Absorbency under load AUL is calculated as follows:

$$\text{AUL [g/g]} = (\text{W}_b - \text{W}_a) / \text{W}_s$$

- where                         $\text{W}_b$  is the mass of the apparatus + gel after swelling,
- 30                              $\text{W}_a$  is the mass of the apparatus + starting weight before swelling, and
- $\text{W}_s$  is the starting weight of dry hydrogel.

35                             The apparatus consists of measuring cylinder + covering plate.

## Gel layer permeability (GLP):

- 40                             The permeability of a swollen gel layer under a confining pressure of 0.3 psi is determined as described in EP-A-0 640 330 as the gel layer permeability (GLP) of a swollen gel layer of superabsorbent polymer, although the apparatus described on page 19 and in Figure 8 of the above-cited patent was modified to the
- 45                             effect that the glass frit (40) was no longer used, the piston (39) is made of the same plastic material as the cylinder (37) and now contains 21 equally sized holes uniformly distributed

0050/980442

over the entire contact surface. The procedure and evaluation of the test method remains unchanged compared to the description in EP-A-0 640 330 and DE-A-195 43 366. The flow rate (g of NaCl solution/sec) is automatically recorded at certain time 5 intervals.

$$GLP = (F_g(t=0)*L_0)/(d*A*WP) \text{ (cm}^3\text{*\text{sec}/g)}.$$

where ( $F_g(t=0)$ ) is the flow rate of NaCl solution in g/sec obtained from a linear regression analysis of the  $F_g(t)$  data of the flow rate conditions by extrapolation to  $t=0$ ,  $L_0$  is the thickness of the gel layer in cm,  $d$  is the density of the NaCl solution in  $\text{g/cm}^3$ ,  $A$  is the area of the gel layer in  $\text{cm}^2$  and  $WP$  is the hydrostatic pressure on the gel layer in  $\text{dyn/cm}^2$ .

15

#### Inventive Example 1

Under adiabatic conditions, a 2 l wide-neck cylindrical reaction flask is charged with 1080 g of completely ion-free water cooled to 15°C, and 430 g of acrylic acid and also 3.4 g of tetraallyloxyethane are dissolved therein. Nitrogen is passed into the monomer solution at a rate of about 2 l/min for about 20 min to lower the oxygen content. At an  $O_2$  content of 1.5 ppm, 7.7 g of a 10% by weight aqueous solution of 2,2'-azobis(2-amidinopropane) dihydrochloride are added, followed, after passing in further  $N_2$  and at an  $O_2$  content of 1.3 ppm, by 2.6 g of a 1% by weight  $H_2O_2$  solution and finally at an  $O_2$  content of 1.0 ppm by the addition of 6.4 g of a 0.1% by weight ascorbic acid solution. The ensuing polymerization, in the course of which the temperature rises to about 75°C, produces a solid gel, which is subsequently subjected to mechanical comminution. 1000 g of the comminuted gel are admixed with 10 g of sodium silicate (27% by weight based on  $SiO_2$  and 14% by weight based on  $NaOH$ ), dissolved in 228.2 g of 50% by weight aqueous sodium hydroxide solution (degree of neutralization of the acrylic acid: 74 mol%), the gel thus obtained is passed twice through a mixing extruder, and the resultant gel particles are dried at above 150°C, ground and sieved.

The product obtained is characterized essentially, inter alia, by the following physical data, all measured in 0.9% by weight NaCl: extractables (1 h value) 2.1%, absorbency under load AUL ( $20 \text{ g/cm}^2$ ) = 20.9 g/g, gel layer permeability (GLP) = 3 ( $\times 10^{-7} \text{ cm}^3\text{sec/g}$ ).

45

100 g of the product thus obtained were sprayed with 10 g of a homogeneous solution consisting of 3.0 g of methanol, 7.0 g of water and 0.1 g of ethylene glycol diglycidyl ether in a powder mixing assembly and heat treated at 140°C for 40 min.

5

The product obtained had the following performance data (measured in 0.9% aqueous NaCl solution):

Centrifuge retention: 33.1 g/g

10 AUL (60 g/cm<sup>2</sup>) : 24.7 g/g

GLP : 60 ( $\times 10^{-7}$  cm<sup>3</sup>sec/g).

#### Comparative Example 1

15 The polymerization is carried out completely analogously to Inventive Example 1, except that no sodium silicate solution is used in the workup to 1000 g of the comminuted gel, instead the neutralization is effected exclusively with 168 g of 50% by weight aqueous sodium hydroxide solution. The product obtained  
 20 differs from the product of Inventive Example 1 in that it has no permeability whatever, i.e., does not allow any fluid to pass through the swollen gel layer and the GLP accordingly has a value of 0 ( $10^{-7}$  cm<sup>3</sup>sec/g). On surface postcrosslinking this product similarly to Inventive Example 1, the postcrosslinked product  
 25 merely has a gel layer permeability (GLP) of 20 ( $10^{-7}$  cm<sup>3</sup>sec/g).

#### Inventive Example 2

A 10 l capacity polyethylene vessel thoroughly insulated by  
 30 foamed plastic material is charged with 3500 g of completely ion-free water at 4°C and 1800 g of acrylic acid are added with stirring. At this point 10.8 g of pentaerythritol triallyl ether are added and the solution is inertized by passing nitrogen into it. This is followed by the addition of the initiator system  
 35 consisting of 2.5 g of 2,2'-azobisisimidinopropane dihydrochloride (dissolved in 20 g of completely ion-free water), 4 g of potassium peroxodisulfate (dissolved in 50 g of completely ion-free water) and also 0.4 g of ascorbic acid (dissolved in 20 g of completely ion-free water), added in succession with  
 40 stirring. The reaction solution is allowed to stand without stirring. The ensuing polymerization, in the course of which the temperature rises to about 90°C, produces a solid gel.

1000 g of the gel thus prepared are mechanically comminuted in  
 45 the presence of a solution of 0.96 g of 27% sodium silicate (from MERCK) in 216.6 g of 50% NaOH and then treated once more in a

mixing extruder. The resultant gel particles are dried at above 150°C and ground.

100 g of the polymer powder thus prepared were sprayed with a  
5 solution of 7 ml of water, 3 g of methanol and 0.20 g of  
2-oxazolidinone in a laboratory mixing assembly and heat treated  
at 175°C for 60 min. The material obtained is characterized by the  
following product data:

10 Centrifuge retention: 24.6 g/g  
AUL (60 g/cm<sup>2</sup>) : 23.9 g/g  
GLP : 8 ( $\times 10^{-7}$  cm<sup>3</sup>sec/g).

Comparative Example 2

15 The polymerization is carried out completely analogously to Inventive Example 2, except that no sodium silicate solution is used in the workup to 1000 g of the comminuted gel, instead the neutralization is effected exclusively with 218.2 g of 50% by  
20 weight aqueous sodium hydroxide solution. The product obtained has, after surface postcrosslinking similarly to Inventive Example 2, a gel layer permeability of merely 4 ( $\times 10^{-7}$  cm<sup>3</sup>sec/g).

Inventive Example 3

25 The polymerization is carried out completely analogously to Inventive Example 2, except that in the course of the workup 1000 g of the comminuted gel are neutralized with a solution of 4.9 g of 35% sodium silicate (27% of SiO<sub>2</sub> + 8% of Na<sub>2</sub>O) in 215.2 g  
30 of 50% by weight NaOH and dried. 100 g of the polymer powder are sprayed with a solution of 0.01 g of sorbitan monococoate and 0.25 g of N-methyloxazolidinone in 10 ml of water in a laboratory mixing assembly and heat treated at 180°C for 45 minutes. The product obtained is characterized by the following data:

35 Centrifuge retention CRC : 31.3 g/g  
Absorbency under load, AUL 60 g/cm<sup>2</sup> : 21.4 g/g  
Gel layer permeability (GLP): 4 ( $\times 10^{-7}$  cm<sup>3</sup>sec/g)

40 Comparative Example 3

The polymerization is carried out completely analogously to Inventive Example 3, except that no sodium silicate solution is used in the workup to 1000 g of the comminuted gel, instead the  
45 neutralization is effected exclusively with 221.5 g of 50% by weight aqueous sodium hydroxide solution. The product obtained

## 10

has, after surface postcrosslinking similarly to Inventive Example 3, the following data:

Centrifuge retention CRC : 31.8 g/g  
 5 Absorbency under load, AUL 60 g/cm<sup>2</sup> : 20.9 g/g  
 Gel layer permeability (GLP): 1 ( $\times 10^{-7}$  cm<sup>3</sup>sec/g)

## Comparative Example 4

- 10 Under adiabatic conditions, a 5 l wide-neck cylindrical reaction flask is charged with 2837 g of completely ion-free water cooled to 10°C, and 1040 g of acrylic acid and also 8.3 g of pentaerythritol triallyl ether are dissolved therein. Nitrogen is passed into the monomer solution at a rate of about 2 l/min for  
 15 about 20 min to lower the oxygen content. At an O<sub>2</sub> content of 1.5 ppm, a solution of 0.52 g of 2,2'-azobis(2-amidinopropane) dihydrochloride in 25 g of completely ion-free water is added, followed, after passing in further N<sub>2</sub> and at an O<sub>2</sub> content of 1.3 ppm, by 12.165 g of a 0.47% H<sub>2</sub>O<sub>2</sub> solution and finally at an O<sub>2</sub>  
 20 content of 1.0 ppm by 16.5 g of a 0.1% by weight ascorbic acid solution. The ensuing polymerization, in the course of which the temperature rises to about 75°C, produces a solid gel, which is subsequently subjected to mechanical comminution. 1000 g of the comminuted gel are admixed with 216.7 g of 50% by weight aqueous  
 25 sodium hydroxide solution (degree of neutralization of the acrylic acid: 74 mol%), the gel thus obtained is passed twice through a mixing extruder and the resultant gel particles are dried at above 150°C, ground and sieved.
- 30 The product obtained is characterized essentially, inter alia, by the following physical data, all measured in 0.9% by weight NaCl:  
 Extractables (1 h value) : 3.7%,  
 Absorbency under load (AUL, 21 g/cm<sup>2</sup>) : 11.1 g/g,  
 Centrifuge retention (CRC) : 33.8 g/g,  
 35 Gel layer permeability (GLP) : 0.1 ( $\times 10^{-7}$  cm<sup>3</sup>sec/g).

Similarly, 1000 g lots of the polyacrylate gel prepared according to Comparative Example 4 were then utilized with varying mixture amounts of sodium silicate/50% NaOH or sodium silicate/alkali  
 40 metal carbonate. In each case sodium silicate from MERCK was used, containing 27% by weight of SiO<sub>2</sub> and 8% by weight of Na<sub>2</sub>O.

Use levels and product data of Preparation Examples 4 to 9 are reported below in Table 1:

Table 1

	Example	Sodium silicate (for 1000 g of gel) g	Alkali (for 1000 g of gel)	pH	CRC g/g	AUL (21 g/cm <sup>2</sup> ) g/g	GLP 10 <sup>-7</sup> cm <sup>3</sup> sec/g
5	Comp. 4	----	216.7 g NaOH 50%	5.83	33.8	11.1	0.1
10	Inv. 4	288.9	124.2 g NaOH 50%	5.65	17.9	20.5	10
	Inv. 5	288.9	110.0 g K <sub>2</sub> CO <sub>3</sub>	5.66	17.1	19.9	8
	Inv. 6	288.9	85.0 g Na <sub>2</sub> CO <sub>3</sub>	5.63	18.0	20.1	11
	Inv. 7	481.5	62.6 g NaOH 50%	5.49	15.0	17.3	32
	Inv. 8	481.5	124.2 g NaOH 50%	7.48	15.4	16.9	28
	Inv. 9	674.0	1.0 g NaOH 50%	5.20	11.9	14.8	45

15 Comparative Example 4a:

100 g of the product obtained according to Comparative Example 4 were sprayed with 10.42 g of a homogeneous solution consisting of 6.0 g of 1,2-propanediol, 2.3 g of water, 2.0 g of a polyamidoamine resin in 15% aqueous solution (RESAMIN® VHW 3608 from Clariant GmbH) and 0.12 g of Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·18 H<sub>2</sub>O in a powder mixing assembly and heat treated at 140°C for 120 min.

25 The product obtained had the following performance data (measured in 0.9% by weight aqueous NaCl solution):

Centrifuge retention: 28.2 g/g  
AUL (60 g/cm<sup>2</sup>) : 24.6 g/g  
30 GLP : 20 (10<sup>-7</sup> cm<sup>3</sup>sec/g).

Further polyacrylate gels prepared according to Comparative Example 4 and neutralized with varying mixture amounts of sodium silicate/50% NaOH were surface postcrosslinked similarly to Comparative Example 4a.

35 Use levels and product data of Preparation Examples 10 to 15 are reported below in Table 2:

Table 2

	Example	Sodium silicate (for 1000 g of gel) g	50% NaOH (for 1000 g of gel) g	CRC g/g	AUL (60 g/cm <sup>2</sup> ) g/g	GLP 10 <sup>-7</sup> cm <sup>3</sup> sec/g
40	Comp. 4a	----	216.7	28.2	24.6	20
45	Inv. 10	9.6	213.6	27.2	24.0	35

	Inv. 11	19.3	210.5	26.7	23.3	41
	Inv. 12	28.9	207.4	24.7	23.2	52
	Inv. 13	38.5	204.3	24.3	22.9	65
5	Inv. 14	48.1	201.3	24.2	22.7	75
	Inv. 15	96.3	155.1	22.7	21.4	87

## Comparative Example 16

10 A 10 l capacity polyethylene vessel thoroughly insulated by foamed plastic material is charged with 3650 g of completely ion-free water at 20°C and 500 g of sodium bicarbonate are suspended therein. 2000 g of acrylic acid are metered into the stirred suspension at such a rate that excessive foaming due to  
 15 ensuing CO<sub>2</sub> evolution is avoided. In the course of the addition, the monomer solution cools down to about 13°C. This is followed by the addition of 3 g of sorbitan monococoate (dispersed in 100 g of completely ion-free water) and also 8.1 g of allyl methacrylate and inertization of the solution by passing nitrogen  
 20 into it. This is followed by the successive addition with stirring of the initiator system consisting of 1.66 g of 2,2'-azobisisamidinopropane dihydrochloride (dissolved in 20 g of completely ion-free water), 3.3 g of potassium peroxodisulfate (dissolved in 150 g of completely ion-free water) and also 0.3 g  
 25 of ascorbic acid (dissolved in 25 g of completely ion-free water). The reaction solution is allowed to stand without stirring. The ensuing polymerization, in the course of which the temperature rises to about 110°C, produces a solid gel.

30 1000 g lots of the gel thus prepared are mechanically comminuted in the presence of a solution containing different amounts of 27% sodium silicate (from MERCK) in 50% NaOH and then treated once more in a mixing extruder. The resultant gel particles are dried in a hot air stream at 170°C and then ground and sieved.

35

Use levels and product data of Preparation Examples 16 to 19 are reported below in Table 3:

Table 3

40	Example	Sodium silicate (for 1000 g of gel) g	50% NaOH (for 1000 g of gel) g	pH	CRC g/g	AUL (35 g/cm <sup>2</sup> ) g/g	GLP $10^{-7}\text{cm}^3\text{sec/g}$
45	Comp. 16	----	18.35	4.4	20.7	10.8	2.5
	Inv. 17	30.8	---	4.3	17.2	15.4	14

Inv. 18	61.7	---	4.3	17.7	15.3	23
Inv. 19	123.3	---	4.5	18.7	15.6	27

## 5 Comparative Example 20

Under adiabatic conditions, a 5 l wide-neck cylindrical reaction flask is charged with 2942 g of completely ion-free water cooled to 10°C, and 1000 g of acrylic acid and also 4.5 g of pentaerythritol triallyl ether are dissolved therein. Nitrogen is passed into the monomer solution at a rate of about 2 l/min for about 20 min to lower the oxygen content. At an O<sub>2</sub> content of 1.5 ppm, a solution of 0.52 g of 2,2'-azobis(2-amidinopropane) dihydrochloride in 25 g of completely ion-free water is added, followed, after passing in further N<sub>2</sub> and at an O<sub>2</sub> content of 1.3 ppm, by 12 g of a 0.47% H<sub>2</sub>O<sub>2</sub> solution and finally at an O<sub>2</sub> content of 1.0 ppm by 16.5 g of a 0.1% by weight ascorbic acid solution. The ensuing polymerization, in the course of which the temperature rises to about 70°C, produces a solid gel, which is subsequently subjected to mechanical comminution.

1000 g lots of the gel thus prepared are mechanically comminuted and neutralized with NaOH (Example 20) or with 27% sodium silicate (from MERCK) (Examples 21-24) and subsequently treated once more in a mixing extruder. The resultant gel particles are dried in a hot air stream at 100°C and then ground and sieved.

Use levels and product data of Preparation Examples 20 to 24 are reported below in Table 4:

30

Table 4

Example	Sodium silicate (for 1000 g of gel) g	50% NaOH (for 1000 g of gel) g	pH	CRC g/g	GLP $10^{-7}\text{cm}^3\text{sec/g}$
Comp. 20	----	75	4.36	29.5	1
Inv. 21	244	---	4.03	15.3	12
Inv. 22	305	---	4.25	18.9	17
Inv. 23	350	---	4.36	19.7	21
Inv. 24	400	---	4.50	20.6	25

## Inventive Example 25

45 Under adiabatic conditions, a 5 l wide-neck cylindrical reaction flask is charged with 2840 g of completely ion-free water cooled to 10°C. 77.0 g of 35% sodium silicate from MERCK (27% by weight

of  $\text{SiO}_2$  + 8% by weight of  $\text{Na}_2\text{O}$ ) and 1040 g of acrylic acid and also 10.4 g of pentaerythritol triallyl ether are dissolved in the initial charge. Silicate and acrylic acid have to be added slowly and in the correct order to avoid precipitating the sodium silicate. Nitrogen is passed into the monomer solution at a rate of about 2 l/min for about 20 min to lower the oxygen content. At an  $\text{O}_2$  content of 1.5 ppm, a solution of 0.52 g of 2,2'-azobis(2-amidinopropane) dihydrochloride in 25 g of completely ion-free water is added, followed after the passing in 10 of further  $\text{N}_2$  at an  $\text{O}_2$  content of 1.3 ppm by 12.165 g of a 0.47%  $\text{H}_2\text{O}_2$  solution and finally at an  $\text{O}_2$  content of 1.0 ppm by 16.0 g of a 0.1% ascorbic acid solution. The ensuing polymerization, in the course of which the temperature rises to about 75°C, produces a solid gel, which is subsequently subjected to mechanical 15 comminution. 1000 g of the comminuted gel are admixed with 198 g of 50% by weight aqueous sodium hydroxide solution, and passed twice through a mixing extruder, and the resultant gel particles are roll dried at a dryer surface temperature of about 180°C, ground and sieved.

20

The product obtained is characterized essentially, inter alia, by the following physical data (all measured in 0.9% NaCl):  
 Absorbency under load (AUL, 21 g/cm<sup>2</sup>) : 21.6 g/g,  
 Centrifuge retention (CRC) : 30.0 g/g.

25

100 g of the product obtained were sprayed with 10.00 g of a homogeneous solution consisting of 3.83 g of 1,2-propanediol, 4.05 g of water, 2.0 g of a polyamidoamine resin in 15% aqueous solution (RESAMIN VHW 3608® from CLARIANT GmbH) and 0.12 g of 30  $\text{Al}_2(\text{SO}_4)_3 \cdot 18 \text{ H}_2\text{O}$  in a powder mixing assembly and heat-treated at 140°C for 120 min.

The product obtained was characterized by the following physical data (all measured in 0.9% NaCl):

35

Centrifuge retention: 26 g/g  
 AUL (60 g/cm<sup>2</sup>) : 24 g/g  
 GLP : 62 ( $10^{-7}$  cm<sup>3</sup>sec/g).

#### 40 Comparative Example 25

The polymerization is carried out completely analogously to Inventive Example 25, except that no sodium silicate is used and instead 214 g of 50% by weight NaOH are used for 1000 g of 45 polymer gel in the subsequent neutralization. Drying and grinding are likewise identical to Inventive Example 25.

15

The product obtained is characterized essentially, inter alia, by the following physical data (all measured in 0.9% NaCl):

Absorbency under load (AUL, 21 g/cm<sup>2</sup>) : 12.0 g/g

5 Centrifuge retention (CRC) : 32.8 g/g.

100 g of the product obtained were surface postcrosslinked likewise completely analogously to Inventive Example 25 to obtain a product characterized by the following physical data (all 10 measured in 0.9% NaCl):

Centrifuge retention: 28 g/g

AUL (60 g/cm<sup>2</sup>) : 24 g/g

GLP : 33 (10<sup>-7</sup> cm<sup>3</sup>sec/g).

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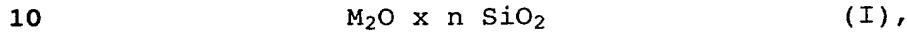
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We claim:-

1. Hydrogels capable of absorbing aqueous fluids, prepared by  
 5 polymerization of olefinically unsaturated carboxylic acids  
 or derivatives thereof, wherefor the polymerization reaction  
 mixture is admixed with an alkali metal silicate of the  
 general formula I



where M is an alkali metal and n is from 0.5 to 4, before,  
 during or after the polymerization reaction and before drying  
 and the hydrogel thus obtained is then dried at elevated  
 15 temperature.

2. Polymers as claimed in claim 1, admixed with alkali metal  
 silicates in amounts of from 0.05% by weight to 100% by  
 weight, reckoned on  $SiO_2$  and based on the total monomer  
 20 weight.
3. Polymers as claimed in claim 1, admixed with alkali metal  
 silicates in amounts of from 1% by weight to 70% by weight,  
 reckoned on  $SiO_2$  and based on the total monomer weight.  
 25
4. Polymers as claimed in any of claims 1 to 3, wherefor the  
 acidic addition polymers are neutralized with mixtures of  
 alkali metal silicates and alkali metal hydroxides.
- 30 5. Polymers as claimed in any of claims 1 to 3, wherefor the  
 acidic addition polymers are neutralized with mixtures of  
 alkali metal silicates and alkali metal carbonates.
6. Polymers as claimed in any of claims 1 to 5, wherefor the  
 35 acidic addition polymers are neutralized to a pH of from 3.5  
 to 9.0.
7. Polymers as claimed in any of claims 1 to 6, wherefor the  
 drying temperatures are in the range from 40°C to 300°C.  
 40
8. Polymers as claimed in any of claims 1 to 7, characterized by  
 a GLP gel permeability of not less than  $25 \times 10^{-7} cm^3 sec/g$  at a  
 polymer pH of from 5.0 to 9.0.

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9. Polymers as claimed in any of claims 1 to 7, characterized by a GLP gel permeability of not less than  $4 \times 10^{-7}$  cm<sup>3</sup>sec/g at a polymer pH of less than 5.0.
- 5 10. The process for preparing the polymers of claim 1 by admixing the polymerization mixture of the polymerization of olefinically unsaturated carboxylic acids or derivatives thereof with an alkali metal silicate of the formula I before, during or after the polymerization reaction and 10 before drying and then drying the thus obtained hydrogel at elevated temperature.
11. Use of the polymers of claim 1 for absorbing aqueous solutions, dispersions and emulsions.
- 15 12. Use of the polymers of claim 1 for producing articles for absorbing aqueous fluids.

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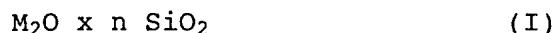
## Crosslinked swellable polymers

## Abstract

5

Hydrogels capable of absorbing aqueous fluids, prepared by polymerization of olefinically unsaturated carboxylic acids or derivatives thereof, wherefor the polymerization reaction mixture is admixed with an alkali metal silicate of the general formula I

10



where M is an alkali metal and n is from 0.5 to 4 before, during or after the polymerization reaction and before drying and the hydrogel thus obtained is then dried at elevated temperature, are used for absorbing aqueous fluids.

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**Declaration**

Page 3 of 4

0050/980442

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# *Declaration, Power of Attorney*

Page 1 of 4

0050/980442

We (I), the undersigned inventor(s), hereby declare(s) that:

My residence, post office address and citizenship are as stated below next to my name,

We (I) believe that we are (I am) the original, first, and joint (sole) inventor(s) of the subject matter which is claimed and for which a patent is sought on the invention entitled

Hydrogels capable of absorbing aqueous fluids

the specification of which

[ ] is attached hereto.

[ ] was filed on \_\_\_\_\_ as

Application Serial No. \_\_\_\_\_

and amended on \_\_\_\_\_.

[x] was filed as PCT international application

Number PCT/EP/99/08850 \_\_\_\_\_

on 18 November 1999 \_\_\_\_\_

and was amended under PCT Article 19

on \_\_\_\_\_ (if applicable).

We (I) hereby state that we (I) have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

We (I) acknowledge the duty to disclose information known to be material to the patentability of this application as defined in Section 1.56 of Title 37 Code of Federal Regulations.

We (I) hereby claim foreign priority benefits under 35 U.S.C. § 119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed. Prior Foreign Application(s)

Application No.	Country	Day/Month/Year	Priority Claimed
19854575.4	Germany	26 November 1998	[x] Yes [ ] No

**Declaration**

Page 2 of 4

0050/980442

We (I) hereby claim the benefit under Title 35, United States Codes, § 119(e) of any United States provisional application(s) listed below.

(Application Number) \_\_\_\_\_ (Filing Date) \_\_\_\_\_

(Application Number) \_\_\_\_\_ (Filing Date) \_\_\_\_\_

We (I) hereby claim the benefit under 35 U.S.C. § 120 of any United States application(s), or § 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. § 112, I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR § 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application.

Application Serial No.	Filing Date	Status (pending, patented, abandoned)
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____

And we (I) hereby appoint:

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Richard L. Treanor,	Registration Number <u>36, 379</u> ;
Robert W. Hahl,	Registration Number <u>33, 893</u> , our (my) attorneys, with full

powers of substitution and revocation, to prosecute this application and to transact all business in the Patent Office connected therewith; and we (I) hereby request that all correspondence regarding this application be sent to the firm of OBLON, SPIVAK, McCLELLAND, MAIER & NEUSTADT, P. C., whose Post Office Address is: Fourth Floor, 1755 Jefferson Davis Highway, Arlington, Virginia 22202.

We (I) declare that all statements made herein of our (my) own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

**Declaration**

Page 4 of 4

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